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FLEXIBLE SUBSTRATE FOR PRINTED WIRING

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16. Abstract:

The invention relates to a very flexible substrate for printed wiring with outstanding solder resistance composed of a product of phenoxy resin and cross-linking resin which is applied to metal etc. without using adhesives.

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FLEXIBLE SUBSTRATE FOR PRINTED WIRING

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1. Title of Invention /483*

Flexible substrate for printed wiring.

2. Scope of Patent Claim

A flexible substrate for printed wiring composed of a blend of phenoxy resin-polyisocyanate-brominated epoxy resin in which the equivalent ratio of the functional groups is hydroxyl group : isocyanate group : epoxy group = 1 : 0.2 to 2 : 0.5 to 3.

3. Detailed Description of the Invention

This invention relates to a very flexible substrate for printed wiring with outstanding solder resistance composed of a product of phenoxy resin and cross-linking resin which is applied to metal etc. without using adhesives.

The requirements of substrates for printed wiring have tended to increase with the development of the electronics industry. Various production methods are used including the copper drawn lamination method, the painting or spraying method, the plating method and electronic photography, but the conventional flexible substrate for printed wiring has the composition as illustrated in figure 3, depending on the demands in the application. It is formed by sticking together a metal layer film (denoted by 4 in figure 3. The following example discusses a typical case using copper foil) which is a conductor and a plastic sheet (10 in figure 3) which is an insulator using adhesive (9 in figure 3). Polyester, polyimide or polyimiamido film are used as the insulating layer. Polyester film is tough, but there are problems including thermal contraction due to heat imposed during soldering etc., and peeling from copper foil or

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warpage. Polyimido and polyimiamido film have superior dimensional stability to heat in comparison with polyester film, but they are not generally used because of their high cost.

In addition, copolymer polyester adhesives such as polyethylene terephthalate or isophthalate are used as the adhesive in the case of polyester film, but adhesives with comparatively low melting points must be used when the adhesion between film and copper foil is to be raised. When that occurs, /484
the adhesive softens due to heat in the soldering operation, and the film peels off from the copper foil or warps since the contraction force of the film cannot be overcome. Consequently, the quality is inadequate, and measures must be undertaken such as the use of expensive solder with a low melting point or minimizing the propagation of heat on the film surface. Thus, the operations become very complex. In the case of polyimide or polyimidoamide film, polyimide or epoxy adhesives are used, but these reduce productivity since long periods of time are rquired for their hardening.

The flexible substrates for printed wiring used today have the various aforementioned problems involving adhesives or solder.

The inventors have conducted thorough examinations into the production of flexible substrates for printed wiring by inexpensive, simple methods to surmount such defects and difficulties, the result of which was the discovery of a flexible substrate for printed wiring capable of withstanding high temperature soldering treatment with strong adhesion combining an adhesive layer and an insulated layer through direct application of a blend primarily of phenoxy resin, polyisocyanate and brominated epoxy resin to copper foil followed by hardening. In addition, the production steps are simplified since an adhesive

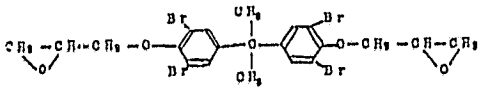
step is unnecessary because the adhesive layer forms directly on the copper foil without using adhesive, and that alone enables production costs to fall.

An example of the production method of the flexible substrate for printed wiring of this invention is explained based on Figure 1, in which phenoxy resin, polyisocyanate and brominated epoxy resin are dissolved in a blended solvent of methyl ethyl ketone/toluene so that the equivalent ratios would be hydroxyl group : isocyanate group : epoxy group = 1 : 0.2 to 2 : 0.5 to 3. Hardening promotors and various types of additives would be added to form a paint. This is supplied to the solvent tank (5) in figure 1. The coating solvent is taken up by the coater roller (1), measured by the metallic roller (2) and is applied to one side of copper foil (4) of 20 to 100 μ through contact of the packing roller (3) and (1) so that the film thickness would be approximately 20 to 200 μ.

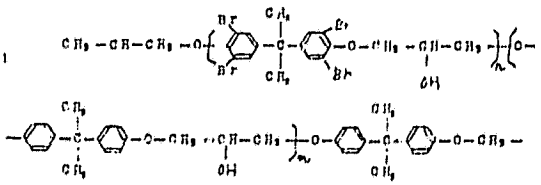
The copper foil may be subjected to etching treatment or chemical treatment on the application side to raise the adhesive strength. The copper foil coated with solvent is introduced into the chamber (6) with a hot wind nozzle for drying where drying and hardening-cross linking are conducted simultaneously, followed by winding in the roller form (7). In the case of imperfect hardening, hardening could be completed by storing the roller for prolonged periods of time in a heated atmosphere. The substrate produced in this fashion would have the structure as illustrated in figure 2. A circuit pattern for wiring would be masked on the substrate produced in this fashion, followed by etching with an aqueous solution of ferric chloride. The unused copper would be eluted followed by water washing and drying, completing the flexible substrate for printed wiring. A flexible substrate for printed wiring with outstanding solder resistance could be formed through combination of phenoxy resin and

polyisocyanate, but the defect is that of easy combustion. In general, an oxygen index (abbreviated O.I.) above 24 is required as a degree of incombustibility in this field, and a combination of the aforementioned two ingredients would be inadequate. Thus, an examination of various fire retardants reveals that the addition of additive fire retardants such as aromatic halides or phosphorous compounds as well as the addition of fire retardants such as antiomony oxide would result in definite improvements, but that the soldering resistance deteriorates, and that a satisfactory substrate cannot be produced. Conversely, the solder resistance could be improved if reactive fire retardants, especially brominated epoxy resins, were used with a range of equivalent ratios of the aforementioned three of hydroxyl group : isocyanate group : epoxy group = 1 : 0.2 to 2 : 0.5 to 3, and the anticipated incombustibility would be achieved. Furthermore, the dimensional stability and pliability would be improved due to the synergism.

The brominated epoxy resins used in this invention would be tetrabromobisphenol A-diglycidyl ether (formula I) as well as the examples cited in formulas II through V.



(Formula I)



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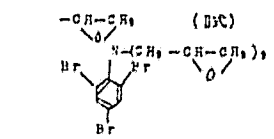

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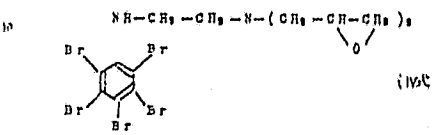
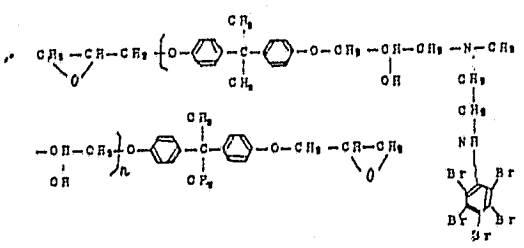


(Formula IV)

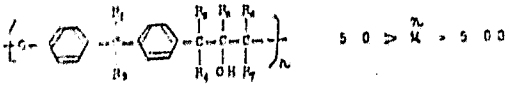


(Formula V)

(However, the hydroxyl groups contained in the epoxy resin are not included in the equivalent calculations.)

Acid anhydrides, benzyl dimethyl amine and tris (dimethylaminomethyl) phenol can be used as hardeners of brominated epoxy resin. In this case, compounds containing active hydrogen such as polyamines, polyamides and polyethyleneimines must be avoided due to their high reactivity with polyisocyanate.

The phenoxy resin used in this invention would be represented as follows.



(Here, R_1 to R_7 represent hydrogen atoms or alkyl groups). Typical examples would be resins represented by $R_{1\sim5} = CH_6$, $R_{5\sim7} =$ H.

The polyisocyanate discussed in this invention signifies compounds containing two or more isocyanate groups per molecule. Typical examples are cited below. Diisocyanate compounds or triisocyanate compounds such as tolylene diisocyanate, diphenyl methane diisocyanate, hexamethylene diisocyanate, 4,4',4"-triisocyanate triphenylmethane; polymethylene polyphenyl isocyanate; isocyanates produced in reactions of isocyanate and amine (for example, trimers of 2,4-tolylene diisocyanate); polyisocyanates in the prepolymer form which are produced through the additive reaction of diisocyanates and triisocyanates with polyesters which have a hydroxyl group at both ends, including polyethylene glycol and monoglycerides; polyisocyanates produced

trolylene diisocyanate and trimethylol propane); polyisocyanates produced through reacting isocyanates and water (for example, polyisocyanate produced through reacting three molecules of hexamethylene diisocyanate and one molecule of water); stable block type polyisocyanate which does not react at room temperature with ingredients which contain hydroxyl groups.

Examples of the hardening promotors which are used include ferric chloride, zinc naphthenate and cobalt naphthenate.

The basis of this invention is a blend of phenoxy resin, polyisocyanate and brominated epoxy resin, but short glass fibers, thermal stabilizers or pigments may be added as required. Short glass fibers below 20 μ in diameter, of 0.5 to 5 mm length and in amounts of 1 to 25 wt.% added would be preferable. In this case, the dimensional stability at high temperatures is further improved in comparison to the absence of addition, and there was virtually no curling or twisting in tests of solder resistance.

A comparison of the resins used in this invention with well-known heat resistant resins such as melamine, phenol or epoxy resins following production of substrates through coating copper foil reveals that the latter are not sufficiently flexible and /486
are unsuited in flexible substrates for printed wiring.

Below, this invention is explained in detail based on actual eamples.

Comparative Example 1

Polyisocyanate (reaction product of three moles of 2,4-tolylene diisocyanate and one mole of trimethylol propane) and tetrabromobisphenol A-diglycidyl ether were blended in phenoxy resin (in the general formula, $R_{1,2}=CH_3$, $R_{3\sim7}=H$, molecular weight

tetrabromobisphenol A-diglycidyl ether were blended in phenoxy resin (in the general formula, $R_{1,2}$=CH_3, $R_{3\sim7}$=H, molecular weight 30,000) at a rate of hydroxyl group : isocyanate group : epoxy group = 1 : 1 : 1, and 3 wt.% of benzyl dimethyl amine based on epoxy resin was added using methyl ethyl ketone/toluene (volumetric ratio 8 : 2) as the solvent. Application to a thickness of 35 μ on copper foil was followed by drying at 150°C x 5 minutes and hardening, thereby producing a substrate with the structure illustrated in figure 2.

The film thickness following drying was 40 μ (Sample No. 1).

Similarly, bisphenol A type epoxy resin (molecular weight approximately 355, 190 equivalents of epoxy) was applied to copper film using boron monoethylamine trifluoride as the hardener, followed by hardening at 180°C x 60 minutes (Sample No. 2). In addition, rubber denatured phenol resin (methyl ethyl ketone solvent) was applied to a thickness of 1 μ on copper foil, pre-hardened at 100°C and then an aqueous solution (Sample No. 4) of methylate methylol melamine (0.2 wt.% magnesium chloride as a hardener) as well as resol type phenol resin (alcoholic solvent, Sample No. 5) were applied, followed by preheating at 100°C and heat hardening for 60 minutes at 150°C, thereby producing the substrate for printed wiring.

Examination of the solder resistance and pliability of these substrates (table 1) reveals that the combination of phenoxy resin-polyisocyanate-brominated epoxy resin produces outstanding pliability and solder resistance.

Table 1

1 試料 No.	2 絶縁層の主成分	3 屈曲性 1)	4 耐半田性 2)
5 1	フェノキシ/ポリイソシアネート/臭素化エポキシ	150回(銅箔破断)	9
6 2	エポキシ樹脂	35回(銅箔破断)	10
7 3	フェノール樹脂	8回(銅箔破断)	11
8 4	メラミン樹脂	25回(銅箔破断)	2(発泡) 13

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1 Sample No.
2 principle ingredient of insulating layer
3 pliability 1]
4 solder resistance 2]
5 phenoxy/polyisocyanate/brominated epoxy
6 epoxy resin
7 phenol resin
8 melamine resin
9 150 times (until destruction of copper foil)
10 35 times (until destruction)
11 8 times (until destruction)
12 25 times (until destruction)
13 (until foaming)

1] Both ends were fixed at sample lengths of 20 mm, and 40 mm of repeated travel were induced between parallel plates 2 mm apart, thereby implementing rubbing tests. The number of times until destruction is indicated. A number above 100 times indicates practical pliability.

2] Changes in shape following storage for 20 seconds in a solder bath at 260°C conforming to JISC 6481 were indicated in the following three stages.
1.. instant loss of shape.
2.. extreme curling as well as change in shape including deterioration and foaming.
3.. loss of substrate flatness due to curling.
4.. development of slight curling.
5.. flatness retained without curling.
Sample size 25 mm x 25 mm

Conversely, epoxy resin, melamine resin and phenol resin lack pliability, and their solder resistance is inferior to that of Sample No. 1. Thus, the resin reaction product used in this invention is clearly superior for flexible substrate for printed wiring in comparison to than conventional heat-resistant resins.

Actual Example 1

The equivalent ratios of isocyanate groups of polyisocyanate (material used in comparative example 1) were altered as illustrated in table 2 in relation to one equivalent of hydroxyl group of phenoxy resin ($R_{1,2}$=CH_6, $R_{3\sim7}$=H, molecular weight approximately 27,000). Tetrabromobisphenol A-dithallinecidyl ether* (3 wt.% of benzyl dimethyl amine in relation to epoxy resin was used as a hardener) was blended in one equivalent of hydroxyl group of phenoxy resin as brominated epoxy resin so as to form one equivalent of epoxy group, and the entire blend was used as methyl ethyl ketone solution. Films of the solutions were applied on a fluorine resin "teflon" plate so as to form a film 40 μ thick. These were dried at 150°C x 3 minutes and hardened. In addition, the solutions were applied to 35 μ thick copper foils at a thickness of 50 μ, producing substrates with the compositions illustrated in figure 2. The properties of the substrates were then evaluated. /487

Table 2

1 試料 No.	2 水酸基1当量に対するイソシアネート基の当量	3 引張り強度 (Kg/mm²)	4 伸度 %	5 オキシジェンインデックス	6 耐半田性 (260℃)
5	0.11	5.2	25	30	1
6	0.2	10.1	16	29	4
7	0.5	15.1	15	27	4～5
8	1.0	14.7	14	26	5
9	2.0	15.9	10	25	5
10	5.0	9.5	7	25	5

1 Sample No.
2 equivalents of isocyanate per equivalent of hydroxyl group
3 tensile strength
4 elasticity
5 oxygen index
6 solder resistance

* phonetic transliteration

Sample No. 5, in which the amount of isocyanate groups was only 0.1 equivalents had insufficient tensile strength (a level above 10 kg/mm^2 would be adequate) and the solder resistance was poor. Conversely, Sample No. 10, which had 30 equivalents of isocyanate, had insufficient elasticity and the pliability was poor. Material with a range of isocyanate groups of 0.2 to 2.0 equivalents enables a balance of mechanical properties to be maintained with good solder resistance and flame retardation. Thus, the material would have outstanding properties as a flexible substrate for printed wiring.

Actual Example 2

Using the phenoxy resin and brominated epoxy resin of actual example 1 as well as the polyisocyanate produced from three molecules of hexamethylene diisocyanate and one molecule of water as the polyisocyanate, a coating solution was produced in which the hydroxyl group of phenoxy resin : isocyanate group of polyisocyanate was constant at 1 : 1 (equivalent ratio) while the amount of brominated epoxy resin added was altered. This was applied to a thickness of 50 μ on a 35 μ copper foil using a roll coater, followed by drying and hardening at 150°C x 3 minutes (structure illustrated in figure 2).

For comparison, the same operations were conducted on brominated epoxy resin alone (Sample No. 17), and the results are illustrated in table 3. Blends in which brominated epoxy resin was not added or in which only 0.2 equivalents were added readily burned, and the magnitude of elongation due to heating was great. Consequently, the defect of curling appeared in the solder-resistance tests.

When there were five equivalents of epoxy group, an excessive figure, the material was incombustible, but the pliability fell which was undesirable. If the epoxy equivalents

ranged from 0.5 to 3 equivalents, the O.I. would be 25 to 29, at which combustion would not readily occur, and the solder resistance due to synergism resulting from combination of the three would be improved, with improved pliability and dimensional stability.

Sample Nos. 13, 14 and 15 were cut into 10 x 10 cm squares, and wiring figures were written on them followed by masking treatment. The unnecessary copper was etched and removed using an aqueous solution of ferric chloride, and a flexible substrate for printed wiring was produced. This was stored for one minute in a solder bath at 260°C, but the pliability was maintained with no deformation in the wiring figure.

The aforementioned indicates that the equivalent ratio of hydroxyl group : isocyanate group : epoxy group = 1 : 0.2 to 2 : 0.5 to 3 would be desirable. /468

Table 3

1	2	3	4	5	6
試料 No.	水酸基1当量に対するイソシアネートの当量	柔軟性	オキシジェンインデックス(O.I.)	耐半田性(260℃)	熱収縮率(250℃)(%)
11	0	95 注1	20	4	−1.0
12	0.5	100 注1	25	4〜5	−0.6
13	0.5	160 注2	25	5	−0.2
14	1.5	140 注2	26.5	5	0.1
15	3	150 注1 / 注2	29	5〜(4)	0.4
16	5	100 注1	30	5〜4	1.0
7 17	臭素化エポキシ樹脂のみ	30 注1		2	−1.5

1 Sample No.
2 equivalents of isocyanate per equivalent of hydroxyl group
3 pliability
4 oxygen index (O.I.)
5 solder resistance
6 thermal contraction rate
7 only brominated epoxy resin

In the results of rubbing tests, #1 denotes those cases in which the resin film cracked and was destroyed while #2 denotes those cases in which the copper foil was destroyed first. #3 denotes the measurements in a heated oven of film resulting from solution on the same teflon plate as that used in actual example 1. A negative thermal contraction rate denotes elongation.

Actual Example 3

Using the coating solution of Sample No. 14 from actual example 2, a coating solution in which 10 wt.%, based on the solid fractions of the sample, of glass fibers of approximately 1 mm length, 6 μ diameter was produced, and this solution was coated on copper foil (35 μ) to a thickness of 50 μ so that the glass fibers would be homogeneously dispersed. This was then hardened at 150°C x 3 minutes. (Sample No. 18). Table 4 illustrates a comparison of the solder resistance and thermal contraction rates of Sample numbers 14 and 18.

1	2				3		
	260	270	280	290	200	220	240
18	5	5～4	5	2	0.10%	0.50%	0.85%
14	5	5	5	5～4	0.05%	0.50%	0.50%

1 Sample No.
2 temperature of solder bath involving solder resistance
3 measurement temperature of thermal contraction rate

Sample No. 18 which contains glass fibers had outstanding solder resistance and dimensional stability.

4. Simple Explanation of the Figures

Figure 1 illustrates one example of the device for coating a solution of phenoxy resin on copper foil.

Figure 2 illustrates a cross section of the flexible substrate for printed wiring of this invention.

Figure 3 illustrates a cross section of the flexible substrate for printed wiring lined with copper which is conventionally used.

1.. coater rollers, 2.. metallic roller, 3.. packing roller, 4.. copper foil, 5.. solution tank, 6.. drying oven, 7.. reel, 8.. insulating layer of this invention, 9.. adhesive layer, 10.. insulating film.

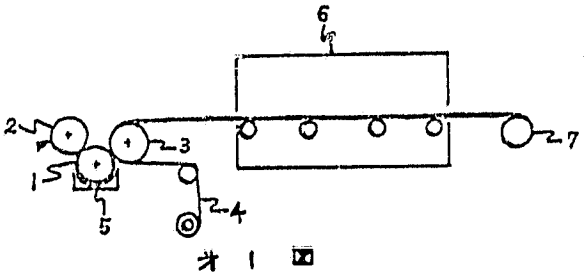

Fig. 1

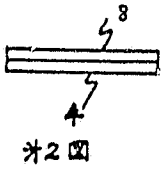

Fig. 2.

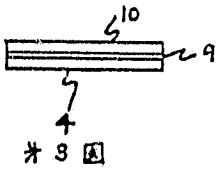

Fig. 3.